

Sol-gel Derived Ag/TiO₂ and Ag-TiO₂ Thin Films for Hydrophilic and Photocatalytic Application

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ABSTRACT: A series of TiO₂ (T), Ag surface doped TiO₂ (SDT) and Ag lattice doped TiO₂ (LDT) thin films were successfully synthesized by sol-gel dip coating process on glass substrates. Ag (0.5 at. %) were use as dopant in TiO₂ thin films and all films were calcined at 500 °C. The physical properties of TiO₂ thin films were carefully studied by using XRD, UV-vis diffuse reflectance spectra (DRS), Field emission surface electron microscopy (FESEM), and Contact Angle measurement, while the chemical states of Ag was determined by X-ray photoelectron spectroscopy (XSP). The photocatalytic activity of the all films was evaluated by photocatalytic degradation of Rhodamine-B (RB) dye in aqueous solution at ambient temperature under UV and visible-light irradiation in the laboratory. The photocatalytic activity shows that the activity of SDT film declined in each successive run, while LDT film activity increased in each subsequent run and reaches plateau on third run. These results indicate that LDT film alters the band gap due to Ag-doping and these are in good agreement with the DRS spectra. Relevant results are discussed as a function of the structure and morphology of LDT thin film, and this controls direct tailoring of the functional response. The high uniformity, transparency, reliability, photocatalytic activity, good adhesion with the substrate and the excellent performance under recycling operation displayed by LDT film make it a good candidate to be considered in new emerging engineering applications.

KEYWORDS: Thin film, TiO₂, Ag/TiO₂(surface doped), Ag-TiO₂(lattice doped), Rhodamine-B dye, Photocatalytic degradation.

I. INTRODUCTION

In the past decades, environmental problems such as air and water pollution have provided the impetus for sustained fundamental and applied research in the area of environmental remediation. Semiconductor photocatalysts offer huge potential for environmental protection procedures. It has been proven that oxide semiconductors such as TiO₂ and ZnO have been recognized as excellent materials for photocatalytic process [1-3]. TiO₂ has been widely used as a primary photocatalyst because of its physical and chemical stability, high oxidative capacity, low cost and ease of availability [4-7]. However, there are two main obstacles for the practical application of TiO₂ photocatalyst: low quantum efficiency and restriction to short wavelength excitation. A common way to enhance the quantum efficiency is to load noble metal on the surface of TiO₂ powder or thin film [8,9] and the deposition of silver has attracted much attention in this perspective [9,10] because of its potential applications. Most of these studies focused on the improvement of photocatalytic activity of TiO₂ under UV irradiation. However, there are some results also reported showing the extension of Ag/TiO₂ wavelength response towards the visible region [9-12]. Presently, most of the methods used for loading silver have been photoreduction. However, the photoreduction needs quite a long time of exposure (more than 1 h in general) and the metal particles are likely to fall off during their repeated utilization. Moreover, photoreduced Ag cannot be highly dispersed on the surface of TiO₂, so that the amount of active sites on the Ag/TiO₂ surface cannot markedly increase, and the electronic structure of TiO₂ photocatalyst cannot change

significantly. To overcome these disadvantages, the introduction of the hybrid sol-gel method to prepare the Ag-modified TiO₂ films is necessary.

In this article, the authors report that doping Ag into the lattices of TiO₂ is more beneficiary than surface doping of TiO₂ with Ag and that it does not only enhances its photocatalytic activity, but also help to alter the band gap of TiO₂. Furthermore, this study also shows that metallic Ag in the Ag/TiO₂ photocatalysts plays another role in contact angle; film induced slightly hydrophobic property. This property defies the dye adsorption on sites of TiO₂ film.

II. EXPERIMENTAL DETAILS

A. SYNTHESIS OF SOLS AND FILMS DEPOSITION

The titania sols were prepared from titanium(IV) isopropoxide precursor (Fluka) and hydrochloric acid (Riedel-de Haen) as a chelating agent, absolute ethanol (EtOH) (Sigma Aldrich) and AgNO₃ (Sigma Aldrich) was used as the precursor for Ag metal ion doping and the concentrations of Ag ions used was 0.5 at.%. In particular, Ti(OiPr)₄ was added to HCl ($n(\text{HCl})/n(\text{Ti}(\text{OiPr})_4) = 3.84$) at room temperature under vigorous stirring. After 5 min, the prepared solution was dissolved in absolute ethanol ($n(\text{EtOH})/n(\text{Ti}(\text{OiPr})_4) = 15.37$) and the resulting solution was subsequently aged at room temperature for 30 min under stirring to get a transparent titania sol. The films were dip-coated onto SiO₂ pre-coated glass slides (25 mm×70 mm×2 mm) at a withdrawal rate of 10 cm/min. For SDT film, Ag species deposited on TiO₂ film where as for LDT film Ag species doped into host sol of TiO₂. In both case Ag species 0.5 at% was kept constant with respect to Ti.

B. CHARACTERIZATION OF FILMS

An X-ray diffractometer (XRD, PANalytical, Holland) with CuKα₁ radiation (1.5406 Å) operated at 40 kV was used to study the crystal structure of T, SDT and LDT films in a wide-angle range (2θ) from 20° to 60° with a step angle of 0.033 using a fully opened X'Celerator detector. The average crystallite sizes were determined from the Scherrer's equation using the broadening of the (1 0 1) anatase peak reflection. The surface morphology investigations were carried out by field emission-scanning electron microscopy (FE-SEM) using FE-SEM, SUPRA 35 VP, Carl Zeiss. Top surface image of films were acquired adopting accelerating voltages from 3 to 15 kV. For the band gap investigation all synthesized films were characterized by DRS spectra (UV-vis absorbance spectra) with a Lambda-950, PerkinElmer Corporation, America. Additionally, the hydrophilic and hydrophobic surface characteristics of synthesized films were evaluated by examining the contact angle (CA) between the film and water droplet. Water CA measurements were performed at room temperature using a horizontal microscope with a protractor eyepiece. To this aim, a Contact Angle Meter (CAM-100), KSV Instrument, Ltd. Finland, was used. In order to confirm the amount of silver within SDT and LDT films, X-ray photoelectron spectroscopy (XPS) spectra were measured using an Escalab MK II (VG Company, UK).

C. PHOTOCATALYTIC TESTING OF FILMS

The photocatalytic activities of TiO₂ films were estimated by studying the degradation of azo dye Rhodamine B (RB) in aqueous solution based on its absorption band at 553 nm (λ_{max}) using a Hewlett-Packard 8453 UV-vis spectrophotometer. The aqueous solution of the dye was prepared with double distilled water. In the present study a batch type continuous flow reactor (5.2 mL/run) with on-line measuring capability of the UV-Vis spectrophotometer was used. The technical details about set-up have already been reported in the previous work [5].

III. RESULTS AND DISCUSSION

A. XRD PATTERNS

Fig. 1 shows the XRD patterns of the T, SDT and LDT films calcined at 500°C for 30 min. As shown in Fig. 1, the X-ray diffraction results confirm that the synthesized materials were TiO₂ of anatase structure and all the diffraction peaks agreed with the reported JCPDS data (Card NO. 29-1360). Evidently, all the reflections belong to anatase phase (peaks appeared at $2\theta = 25.4^\circ, 38.1^\circ, 48^\circ, 54.1^\circ$ and 55.2° correspond to (101), (004), (200), (105) and (211) reflections, respectively) and no additional reflection belonging to Ag species is observed in SDT and LDT films. This result indicates that the % of Ag species was too small with respect to Ti. The average crystallite size determined

from the Scherrer's equation using the broadening of the (101) anatase peak for T, SDT and LDT films is in the range of 10-12 nm.

B. UV-VIS ABSORPTION SPECTRA

Fig. 2 shows the UV-vis absorption spectra of T, SDT and LDT films after calcination before use. It can be seen from Fig. 2, that all films show good photo-response and absorption in ultraviolet region. In comparison with T film, it is observed that the photo-response and absorption intensity of SDT and LDT films in ultraviolet and visible light region are higher than those of T. However the LDT film exhibits much continuous and stronger absorption band in the range of 400-800 nm compare to SDT which could be attributed firstly to Ag species enter into the host Ti lattice and LDT film enhance light absorption in the large region from 400 to 800 nm, which is favourable to the enhancement of photocatalytic activity of TiO₂ in wastewater purification. The estimated band gap of T, SDT and LDT are 3.12eV, 3.16eV and 3.01eV respectively, which are well demonstrated in the photocatalytic results.

C. FE-SEM analysis:

Fig. 3 depicts FE-SEM images of the T, SDT and LDT films. All images show the surface morphology of films exhibiting smooth, uniform and non-ill-defined surfaces. This revealed a homogeneously spherical nano crystallite structure with clear interstices between the crystallites. It can be clearly seen from Fig. 3 that the size of nanocrystalline titania is between 10 and 12 nm, which agrees with average crystallite size determined from the Scherrer's equation using the broadening of the (101) anatase XRD peak.

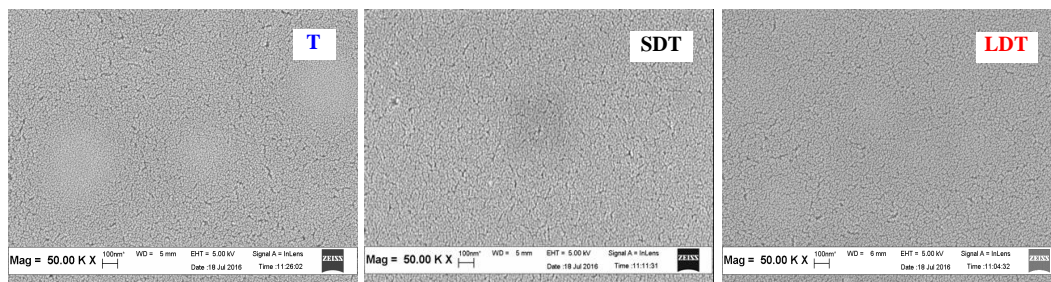


Fig.3. FE-SEM images of the T, SDT and LDT films

D. XPS ANALYSIS

The surface composition of SDT and LDT films were analysed by X-Ray Photoelectron Spectroscopy (XPS) in order to get information on the chemical state of the different species. In particular, the aim of the analysis was to confirm whether the Ag dopant was homogeneously distributed in the titania host matrix or not and to determine the chemical state (Ag⁰ or Ag⁺). Fig. 4. Shows the XPS spectrograph of SDT and LDT films. In both spectra, Ag, C, Ti and O are well evident. As far as the other elements are concerned, the considerable amount of carbon detected on the surface has to be ascribed to adventitious contamination carbon. The chemical state of the species reveals that the binding energy (BE) values for the Ti2p region range, for all the analyzed samples lie in the interval 458.2-458.7 eV, which are values typical of titania. It should however be underlined that upon sputtering, the Ti2p peak broadens, due to a partial reduction of Ti(IV) to lower oxidation state of the species. This can in turn be ascribed to a preferential sputtering of oxygen, leading to oxygen depletion and consequently to a reduction of the metallic species. Concerning oxygen, the O1s region, peaked at 529.5-530.0 eV, values are typical of O1s in titania, which shows a shoulder at higher BE (about 531.0-531.7 eV), and this can be ascribed to OH surface groups. The silver Ag3d region, displays the typical doublet with the main Ag5/2 component and the Ag3/2 component shift of 6 eV at higher BE. By considering the BE of silver on the surface, where the amount of Ag has its highest values, regardless of the sample and the thermal treatment, these have a value ranging between 367.0 and 367.3 eV, which witnesses the presence of silver in its Ag⁺ oxidation state, whereas the presence of metallic silver, characterised by higher BE values (368.1-368.3 eV) can be ruled out. Although silver is easily reduced when in contact with titania, XPS results clearly show the presence of Ag⁺ in LDT film, which can be formed on the titania surface in the course of the oxidation of photoreduced silver Ag⁰ in case of SDT film.

E. CONTACT ANGLE MEASUREMENTS

Fig. 5 depicts the change in contact angle (CA) values for the T, SDT and LDT films as a function of UV illumination time. Prior to contact angle measurements, all calcined films were rinsed with deionised water and aged at room temperature for 30 min. After aging, both films were UV irradiated for 1 h and left in the dark place for 48 h to turn into hydrophobic nature. In fact, the starting values for the T film are appreciably higher (~58°) than for the SDT and LDT film (~55° and ~51°) respectively, indicating a more hydrophilic character of the T film. Nevertheless, it is interesting to observe that upon UV irradiation, the CA for T film undergo a considerable faster decrease from the initial CA values of ~58° to ~23° within 20 min, and this is an indication of increase in the hydrophilicity of the T film than SDT and LDT which respectively dropped from ~55° to ~30° and ~51° to 27° within 20 min. From the results it is clear that the Ag doping assisted the hydrophilicity-resistance in SDT and LDT films. However LDT film shows more hydrophilic nature than SDT film. Furthermore, the irradiation with UV-light induced additional decrease of water contact angles of T film, suggesting an enhanced hydrophilicity of T film.

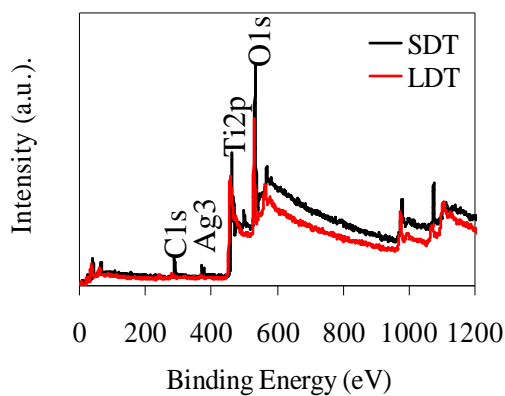


Fig. 4. XPS spectra of SDT & LDT film

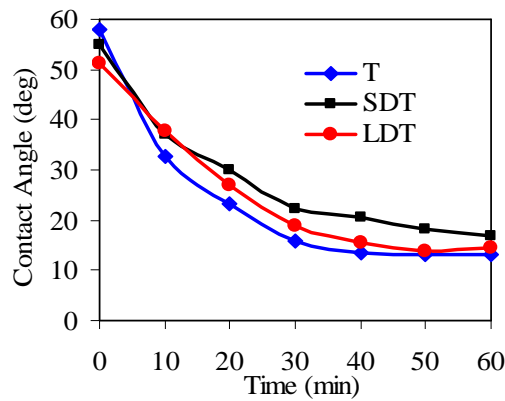


Fig. 5. C.A. Measurement T, SDT and LDT film

F. PHOTOCATALYTIC ACTIVITY AND ITS REPRODUCIBILITY

The photocatalytic activity of synthesized TiO₂ thin films was evaluated by the degradation of an azo dye RB under UV light irradiation with on-line measurement system.

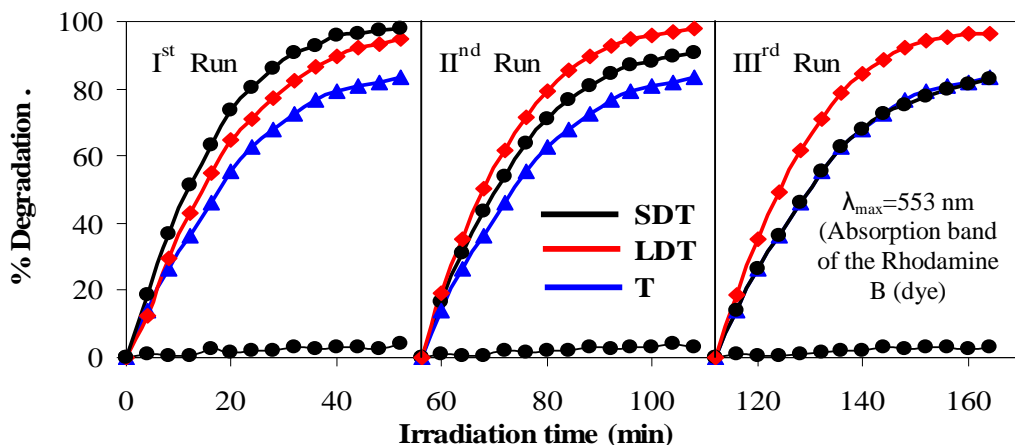


Fig. 6: Photocatalytic activity and its reproducibility

Fig. 6 (Ist Run) depicts the photocatalytic degradation of the azo dye RB (conc. 20 mg L⁻¹) for dip-coating prepared films (T, SDT, LDT) and Blank as a function of UV light irradiation time. In the first run, it can clearly be seen that the SDT thin film exhibited an excellent photocatalytic activity compared to T and LDT films. This performance of SDT film is directly pointing to the fast electron trapping from TiO₂ surface compare to T and LDT films. Due to this trapping the SDT film shows slightly better photocatalytic activity than LDT and T films in the Ist run. The reproducibility of the photocatalytic activity of the TiO₂ films was also confirmed by three repetitive photocatalytic degradation cycles of dye RB with corresponding spectrophotometric measurements. The results in Fig. 6 (IInd and IIIrd Runs) show that there are significant changes in the photocatalytic degradation curves for SDT film, whereas LDT film exhibited an increase in activity in IInd and IIIrd runs compared to SDT, and T seems to be constant in activity in each run. Results of LDT film show the reproducibility, stability and reliability of the sol-gel synthesized anatase TiO₂ film compared with SDT film. The consistency in activity of LDT film in each run indicates that Ag species are introduced into host matrix of TiO₂, and as a result the band gap of TiO₂ alter. This result is in accordance with the red shift results of UV-vis absorption spectra.

IV. CONCLUSION

The present work explores the potentialities of different TiO₂ films prepared with surface and lattice Ag-doping. The principal advantages of LDT are uniformity, transparency, reliability and most importantly reproducibility, which are not present in the SDT and T films. The most important outcomes of the present work are: (i) though doping in photocatalysis is important, it is not sufficient because it should produce lattice distortion which should eventually result in band gap alteration and (ii) surface doped photocatalyst does not show consistency in reproducibility.

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